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KINETICS OF LOCALIZED CORROSION OF AUSTENITIC STAINLESS STEELS PART 1 - PITTING IN FERRIC CHLORIDE SOLUTIONS

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CORROSION SCIENCE SECTION

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KINETICS OF LOCALIZED CORROSION OF AUSTENITIC STAINLESS STEELS
PART 1 - PITTING IN FERRIC CHLORIDE SOLUTIONS

by

Emily Powers and Robert Brigham

ABSTRACT

In exposure tests in ferric chloride solutions, austenitic stainless steels exhibited pit growth kinetics which followed a $t^{1/3}$ rate law indicative of a constant local corrosion current at each individual pit. The rate of pit growth was shown to be under cathodic control.

LABORATOIRES DE RECHERCHE EN MÉTALLURGIE PHYSIQUE
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CINÉTIQUE DE LA CORROSION LOCALISÉE D'ACIERS INOXYDABLES AUSTÉNITIQUES PARTIE 1 - FORMATION DE PIQÛRES DANS DES SOLUTIONS DE CHLORURE FERRIQUE

par

Emily Powers et Robert Brigham

RÉSUMÉ

Lors des essais d'exposition dans des solutions de chlorure ferrique, les aciers inoxydables austénitiques ont montré des vitesses de croissance des piqûres qui suivaient une équation de vitesse de $t^{1/3}$ dénotant un courant constant de corrosion locale à chaque piqûre individuelle. On a démontré que la vitesse de croissance des piqûres était sous contrôle cathodique.

INTRODUCTION

Pit initiation in austenitic stainless steels in oxidizing chloride solutions is now known to occur within well defined boundaries of temperature and alloy chemistry. Early work in this field, based on results of ferric chloride exposure tests (1), quantified pit initiation in terms of a go/no-go temperature, i.e., a critical pitting temperature (CPT). The beneficial effects of molybdenum alloying additions on suppressing pit initiation were also clearly demonstrated (2). However, because it is not always economically feasible to specify a stainless steel which falls within the boundaries of immunity to pit initiation, a knowledge of the rate of pit growth would facilitate an estimate of useful life in terms of time to perforation.

The general rate equation takes the form:

$$d = A(t-t_o)^m$$

where d is the pit depth, A is a constant, t is time, t_o is incubation period and m is the rate exponent.

For stainless steels under potentiostatic control, Hunkeler and Boehni (3) found m = 0.53 to 0.7 for 430, 304 and 316L. They postulated a diffusion controlled rate of pit formation for which, ideally, m = 0.5. Similarly, from experiments with 304 in a rotating electrode configuration, Sato et al (4) found m = 0.5 and concluded "that the field-assisting ionic migration through the pit is rate limiting". On the other hand, Hisamatsu et al (5) found that with 304, m = 1 at 600 mV_{SCE}, although m decreased at more active potentials. Tousek (6) found for the same steel that m = 0.6 to 0.8 with a preferred value of 0.66. He concluded that the dissolution of steels in pits is not controlled by diffusion, but by electrochemical reaction.

Recently, Tousek (7) reviewed the behaviour of a number of metal/electrolyte systems at various potentials where pitting occurs and found a wide range of rate laws. In many cases - although not for stainless steel in chloride solution - the local current density at each pit was found to be constant with time. In all cases, the systems were under potentiostatic control and the exposure times were short - approximately 5 min. No long-term free corrosion data for stainless steels have been reported in the form of a rate law. However, for aluminum alloys, Godard (8) found m = 0.33 for 3003 alloy

in a 12-week exposure as well as for 5052 alloy in a 22-year exposure in fresh water.

This study is an attempt to determine the pit growth kinetics of stainless steels under free corrosion conditions in an aggressive chloride environment for intermediate times (up to 144 h) and to evaluate the effects of variables, such as alloy composition and temperature, which might be expected to influence kinetics.

EXPERIMENTAL

Coupons of 304, 316L and 904L austenitic stainless steels (analyses in Table 1) approximately 40 x 40 mm were sheared from sheet of 3.2, 2.0 and 2.0 mm thickness, respectively. Metal surfaces were abraded with 600 grit SiC and the coupons were exposed horizontally. In all cases, the test solution consisted of 800 mL 10% $FeCl_3$ (200 g $FeCl_3.6H_2O$ in 1 L of distilled water) at temperatures ranging from slightly above the CPT for each alloy to 55°C and, in the case of 904L, to 70°C, controlled to ±1°C by constant-temperature baths.

After immersion, the coupons were thoroughly cleaned and the depths of all pits were measured with a needle probe attached to a digital indicator accurate to 0.001 mm. The value for the deepest pit was recorded. Pits which were connected to edge or end grain attack were not measured. Weight losses and areas were also measured. Because the horizontal coupons pitted on the top surface only, the area of that surface rather than the immersed area was used to calculated weight loss per unit area.

RESULTS AND DISCUSSION

Based on earlier pit initiation studies (1,2), variables such as temperature and alloy composition were expected to influence pit growth rates. However, the results were not consistent with this prediction. For example, Fig. 1 shows maximum pit depth results for the 42 coupons of 304 stainless steel exposed in 10% $FeCl_3$ for up to 144 h. These data show considerable scatter but it is evident that different temperatures in the range 10 to 55°C result in no systematic trends to a maximum pit depth. The data are bounded by the straight line in Fig. 1 described by:

$$d = 0.58\ t^{1/3}$$

This rate equation, delineating the boundary of the maximum pit depth data, is the equation for the growth of an individual pit, i.e., the deepest pit in each coupon.

In Fig. 2 and 3, maximum pit depth data as a function of time are shown for 316L and 904L stainless steels, respectively. In both cases, the absence of temperature dependency agrees with the behaviour noted in Fig. 1 for 304 stainless steel. In addition, the rate equations for the growth of the deepest pit in the three steels are identical. In Fig. 1, 2 and 3, arrows on data points indicate perforation. In contrast to the pit growth kinetics in Fig. 1 to 3, Fig. 4 shows that weight loss of coupons with an array of pits is a linear function of time. In this case, both temperature and alloy composition have considerable influence but, surprisingly, 304 and 316L show similar weight losses. This behaviour is demonstrated more clearly in Fig. 5 where data points indicate the degree of scatter observed. The higher weight losses result primarily from a higher density of pits, but also from a higher degree of edge attack on the coupons.

The data in Fig. 1 to 5 help to clarify the pit growth phenomenon. For the growth of an individual pit, the anodic reaction is:

$$M \text{ ----> } M^{n+} + ne^-$$

which, in ferric chloride solution, is driven by the external cathodic reaction

$$Fe^{+++} + 1e^- \text{ ----> } Fe^{++}$$

The anodic reaction rate is known from polarization curves to be influenced by the composition of the anode and the temperature. Because Fig. 1, 2 and 3 show that the growth kinetics of individual pits are influenced neither by alloy composition nor by temperature, it is clear that the kinetics of each individual pit are under cathodic control. Further, the $t^{1/3}$ growth rate for individual spherical or hemispherical pits suggests that the local corrosion current is constant for each pit. Conversely, the growth kinetics of an array of pits (as indicated by weight loss measurements) indicate that

the aggregate behaviour is not simply the sum of the growth kinetics of individual pits but includes an element of anodic control.

To verify further that the growth of individual pits is under cathodic rate control, a series of experiments was performed on 304 at 25°C in Fe^{++}/Fe^{+++} mixtures of 1:1 and 10:1, but with Cl^- concentrations equal to that of 10% $FeCl_3$. To ensure pit nucleation, coupons were exposed in 10% $FeCl_3$ for 1/2 h before adding the $FeCl_2$ solution in the required proportions. The results are shown in Fig. 6. In the 1:1 mixture of Fe^{++}/Fe^{+++}, the growth rate of the deepest pit has been reduced to:

$$d = 0.48\ t^{1/3}$$

This decrease in rate in the less oxidizing Fe^{++}/Fe^{+++} mixture confirms that the growth of the deepest individual pit is under cathodic control. It should be noted that in 10:1 Fe^{++}/Fe^{+++} mixtures, nucleated pits would not propagate and the maximum depths of approximately 0.4 mm are consistent with the initial 1/2 h exposure in 10% $FeCl_3$.

The observation that nucleated pits did not grow in a 10:1 Fe^{++}/Fe^{+++} mixture is surprising because the electrochemical potential of the solution measured on bright platinum is +375 mV_{SCE}. This potential is well above the anticipated value of the protection potential for 304 stainless steels.

CONCLUSIONS

1. Individual pits in stainless steel in 10% $FeCl_3$ solutions follow a $t^{1/3}$ rate law indicative of a constant local corrosion current for each pit.
2. Growth kinetics of individual pits are under cathodic control and consequently, insensitive to the composition of the stainless steels.

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Table 1 - Chemical analysis of steel (wt %)

Steel	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N
304	.065	.59	1.75	.03	.005	18.5	8.4	0.23	NA	NA
316L	.015	.39	1.57	.020	.002	17.1	11.2	2.23	NA	NA
904L	.015	.45	1.58	.028	.003	20.0	24.5	4.34	1.60	.073

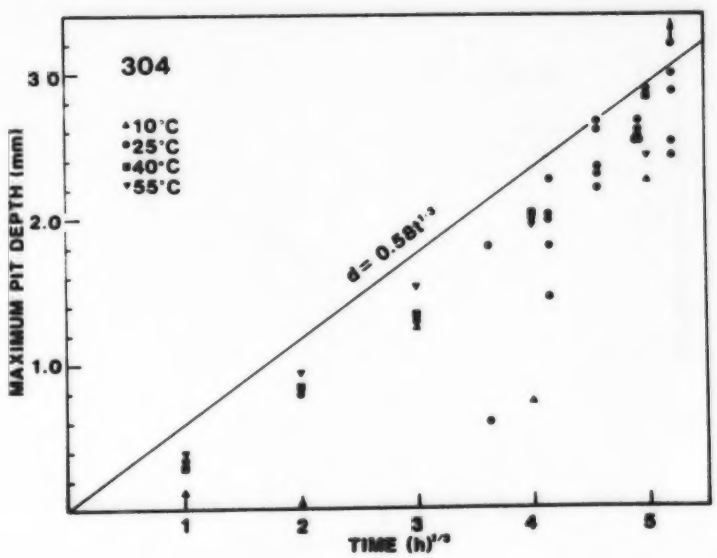

Fig. 1. Maximum pit depth in 304 stainless steel as a function of exposure time in 10% $FeCl_3$. (neg 13767)

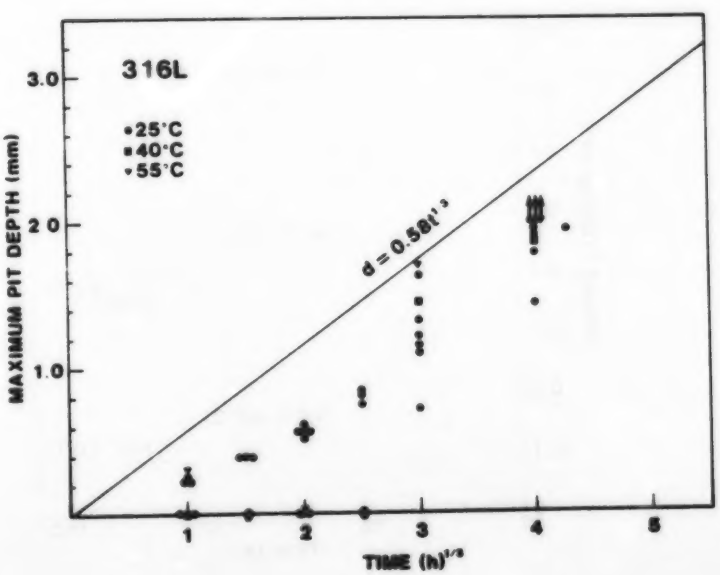

Fig. 2. Maximum pit depth in 316L stainless steel as a function of exposure time in 10% $FeCl_3$. (neg 13771)

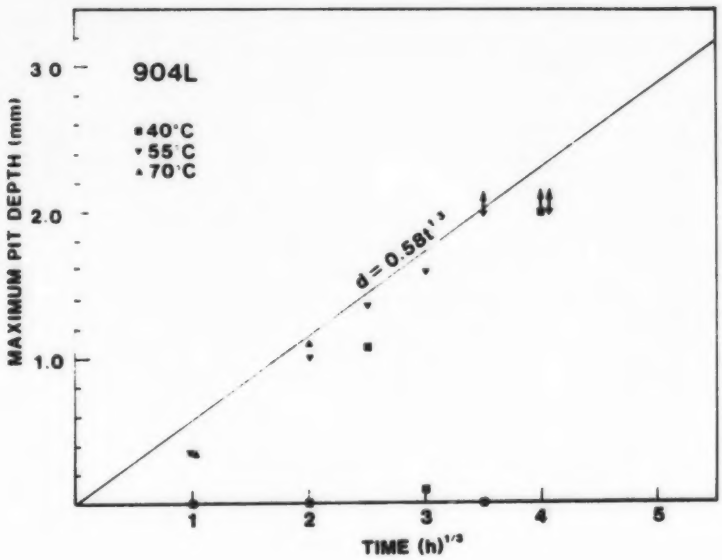

Fig. 3. Maximum pit depth in 904L stainless steel as a function of exposure time in 10% $FeCl_3$. (neg 13772)

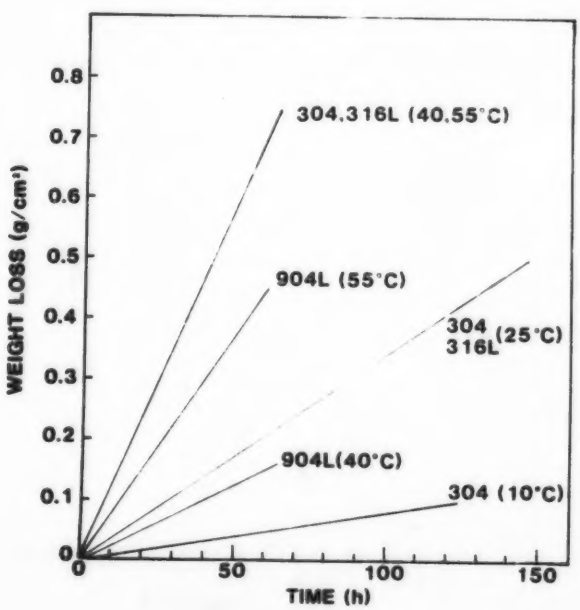

Fig. 4. Weight loss in 304, 316L and 904L stainless steels as a function of exposure time in 10% $FeCl_3$. (neg 13769)

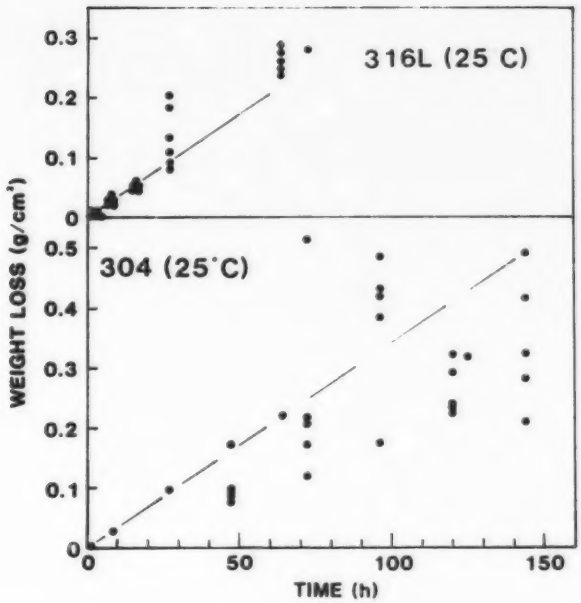

Fig. 5. Comparison of the weight loss in 304 and 316L stainless steels as a function of time in 10% $FeCl_3$. (neg 13768)

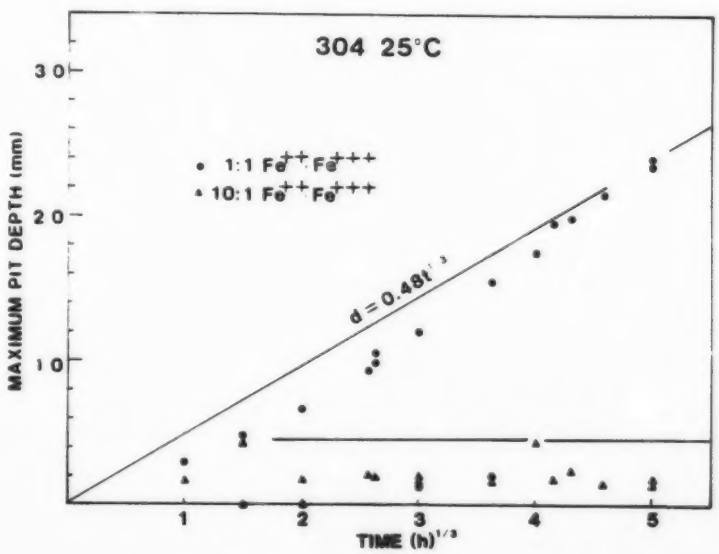

Fig. 6. Maximum pit depth in 304 stainless steel as a function of exposure time in $FeCl_2/FeCl_3$ mixtures with Cl^- concentration equal to that of 10% $FeCl_3$. (neg 13770)